

Heats, Equilibrium Constants, and Free Energies of Formation of the C₃ to C₅ Diolefins, Styrene, and the Methylstyrenes¹

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For the C₃ to C₅ diolefins, styrene, and the methylstyrenes, values are presented for the following thermodynamic properties to 1,500° K: Heat-content function, free-energy function, entropy, heat content, heat capacity, heat of formation from the elements, free energy of formation from the elements, and logarithm of the equilibrium constant of formation from the elements. Equilibrium constants and concentrations are given in tabular and graphical form for some reactions of isomerization and dehydrogenation.

I. Introduction

As part of the work of the American Petroleum Institute Research Project 44 at the National Bureau of Standards and the University of California, values have been compiled for the thermodynamic properties, in the gaseous state to 1,500° K, of the heat-content function, free-energy function, entropy, heat content, heat capacity, heat of formation, free energy of formation, and logarithm of the equilibrium constant of formation for the C₃ to C₅ diolefins, styrene, and the methylstyrenes. Calculations have also been made of the free energies and equilibrium constants of a number of reactions involving isomerization and hydrogenation of these compounds.

II. Constants

The values of the constants used in the present calculations are as follows [1, 2]:⁶ The calorie

used is the conventional thermochemical calorie defined as 4.1840 absolute joules; the absolute temperature of the ice point is 273.160 ± 0.010° K; the value of the radiation constant, hc/k , is 1.43847 ± 0.00045 cm deg; the gas constant is 1.98719 ± 0.00013 cal/deg mole. Values of other constants related to these are given in references [1, 2].

III. Heat-Content Function, Free-Energy Function, Entropy, Heat Content, and Heat Capacity

1. C₃ to C₅ Diolefins

For propadiene (allene), the thermodynamic functions were computed by using the following: The assignment of frequencies given by Thompson and Harris [3], which differs slightly from previous assignments [4, 5], two equal moments of inertia (9.82×10^{-39} g cm²) recalculated from the spectral data on the rotational fine structure [6], a third moment of inertia (0.575×10^{-39} g cm²) assumed to be equal to that of ethylene [7], and a symmetry number of four. The foregoing moments of inertia correspond to the following dimensions of the molecule of propadiene, which agree well with those obtained from measurements of electron diffraction [8]: C=C, 1.34 Å; C—H, 1.07 Å; H—C—H angle, 120°. The uncertainty in the

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⁶ Figures in brackets indicate the literature references at the end of this paper.

calculated values of the thermodynamic functions is estimated to be about 0.2 cal/deg mole at the lower temperatures and somewhat greater at the higher temperatures because of the neglect of vibrational anharmonicities. The values of heat capacity calculated for propadiene in the present investigation agree very well with the experimental data that have been reported [4, 9, 10]. Some values of entropy previously calculated for propadiene by other workers [11, 12], however, differ markedly, for some unknown cause, from those given in the present report.

For 1,2-butadiene, the thermodynamic functions were computed by using the following: The assignment of frequencies given by Szasz, McCartney, and Rank [13]; moments of inertia based on the same corresponding dimensions as for propadiene, together with additional dimensions of 1.54 Å for C—C and 1.09 Å for H—CCH₃, giving $I_1 = 2.819 \times 10^{-39}$, $I_2 = 20.31 \times 10^{-39}$, and $I_3 = 22.03 \times 10^{-39}$ g cm²; a reduced moment of inertia for the methyl rotation of 4.78×10^{-40} g cm² corresponding to $I_{\text{CH}_3} = 5.30 \times 10^{-40}$ g cm²; and a potential barrier restricting internal rotation of 1,800 cal/mole, which was selected to fit the experimental value of entropy of gaseous 1,2-butadiene at 273.25° K reported by Aston and Szasz [14], including a calorimetrically measured entropy of vaporization. The potential barrier from the present calculations is slightly different from that reported by Aston and Szasz [14] because of the difference in the molecular dimensions used in the respective calculations. As might be expected, the potential barrier for 1,2-butadiene is about the same as that for propylene. The assignment of vibrational frequencies made by Szasz, McCartney, and Rank [13] was tested by calculating approximate product ratios for methyl substitutions of the type used by Pitzer and Scott [15], in which calculations the values of the product ratios for 1,2-butadiene agree very well with those for the methylbenzenes. This agreement offers considerable confirmation of the assignment of frequencies for 1,2-butadiene.

For 1,3-butadiene, the available spectroscopic and other molecular data appear to be satisfactorily represented by the values of the thermodynamic functions calculated by Aston, Szasz, Wooley, and Brickwedde [16], and their values for the heat-content function, free-energy function, and heat capacity were used in the present

calculations. However, it should be noted that the available spectroscopic and other molecular data are not sufficient to confirm the correctness of the details of their molecular model of 1,3-butadiene.

For the pentadienes, the available thermal, spectroscopic, and other molecular data are either insufficient or too uncertain to permit a satisfactory statistical treatment at the present time. However, by taking advantage of regularities in the properties of related compounds, thermodynamic functions for the pentadienes may be calculated by suitable combination of the thermodynamic functions for other compounds for which the appropriate values have already been calculated [15, 17, 18, 19]. For such calculations by the method of increments, the following equations were used to evaluate the thermodynamic functions for the seven pentadienes:

$$G(1,2\text{-pentadiene}) = G(1\text{-butene}) + (1) \\ G(1,2\text{-butadiene}) - G(\text{propylene}).$$

$$G(2,3\text{-pentadiene}) = 2G(1,2\text{-butadiene}) - (2) \\ G(\text{propadiene}) - R \ln 8.$$

$$G(3\text{-methyl-1,2-butadiene}) = G(\text{isobutene}) + (3) \\ G(1,2\text{-butadiene}) - G(\text{propylene}).$$

$$G(\text{cis-1,3-pentadiene}) = G(\text{cis-2-butene}) + (4) \\ G(1,3\text{-butadiene}) - G(\text{propylene}) + R \ln 4.$$

$$G(\text{trans-1,3-pentadiene}) = G(\text{trans-2-butene}) + (5) \\ G(1,3\text{-butadiene}) - G(\text{propylene}) + R \ln 4.$$

$$G(2\text{-methyl-1,3-butadiene}) = G(\text{isobutene}) + (6) \\ G(1,3\text{-butadiene}) - G(\text{propylene}) + R \ln 4 - 0.3.$$

$$G(1,4\text{-pentadiene}) = 2G(1\text{-butene}) - (7) \\ G(\text{propane}) - R \ln 4.$$

In the foregoing equations, G represents the heat content function, the negative of the free energy function, or the heat capacity. The constant terms, $R \ln 8$, etc., appearing, respectively, in eq 2, 4, 5, 6, and 7, are corrections for the symmetry number and are to be used for the negative of the free-energy function, $-(F^\circ - H_0^\circ)/T$, but not for the heat-content function or the heat capacity. The values of the thermodynamic functions used for the calculations represented by eq 1 to 7, inclusive, are from the following: Propane [18]; propylene, 1-butene, *cis*-2-butene, *trans*-2-butene, and isobutene [19].

There are now available a number of checks on the accuracy of the increment method for calculating thermodynamic functions, as illustrated by eq 1 to 7, inclusive. Some confirmation of the increment method has already been reported for certain alkylbenzenes [15, 20] and for certain alkylecyclohexanes [17, 21].

In 1946, values of the thermodynamic functions for 2-methyl-2-butene were calculated [22] by means of the relation

$$G(2\text{-methyl-2-butene}) = \frac{2}{3} G(\text{cis-2-butene} + \text{trans-2-butene} + \text{isobutene}) - G(\text{propylene}) + R \ln 4. \quad (8)$$

This yielded 80.90 cal/deg mole for the standard entropy in the gaseous state at 25° C, which is to be compared with the value 80.92 subsequently available from the experimental work of Todd, Oliver, and Huffman [22], and Huffman and Scott [23]. The calculated value for the heat capacity of gaseous 2-methyl-2-butene is about 1 percent higher than the experiment value that has recently become available [23].

Before the recent experimental work on 1,2-butadiene became available [14], the authors had calculated the thermodynamic functions of 1,2-butadiene by the method of increments with what now appear to be excellent results, using the equation

$$G(1,2\text{-butadiene}) = G(\text{allene}) + G(\text{propylene}) - G(\text{ethylene}). \quad (9)$$

The standard entropy of gaseous 1,2-butadiene at 25° C was calculated by the method of increments to be 69.7 cal/deg mole, which is to be compared

with the new calculated value of 70.03 ± 0.20 cal/deg mole.

There is an experimental entropy available for comparison with our result for 2-methyl-1,3-butadiene (isoprene). The experimental value, 75.2 ± 0.3 , [24, 25] is 0.5 cal/deg mole lower than the value given by the increment equation without the term -0.3 . Although this difference is well within the expected uncertainties of the method, the additional constant term (-0.3) was added to the increment equation, in order to have better agreement with the isoprene experimental value at 298.16° K. Presumably, this change gives better extrapolated values at higher temperatures.

In connection with the calculation of the thermodynamic functions of the pentadienes by the method of increments, it is estimated that the over-all uncertainty is about 1 cal/deg mole at room temperature and greater at higher temperatures, the values for 1,4-pentadiene being particularly uncertain. However, the differences between values of the thermodynamic functions at given temperatures are more significant than the over-all uncertainties.

The resulting values of the thermodynamic functions for the diolefins, C_3 to C_5 , are given in tables 1 to 5, inclusive, which give values of the following properties, respectively, from 0° to 1,500° K: Heat-content function, free-energy function, entropy, heat content, and heat capacity. The value of the entropy is obtained as the value of the heat-content function less the value of the free-energy function, and the value of the heat content is obtained by multiplying the value of the heat-content function by the temperature.

TABLE 1. *Values of the heat-content function, for the ideal gaseous state, to 1,500° K, for the C_3 to C_5 diolefins*

Compound (gas)	For- mu- la	Temperature in ° K														
		0	298.16	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400	1,500
Heat-content function, $(H^\circ - H_0^\circ)/T$, in cal/deg mole																
Propadiene (allene)-----	C_3H_4	0	10.12	10.15	11.54	12.94	14.28	15.51	16.66	17.71	18.68	19.57	20.40	21.17	21.88	22.54
1,2-Butadiene-----	C_4H_6	0	12.92	12.96	15.07	17.16	19.15	21.01	22.74	24.34	25.82	27.18	28.44	29.62	30.70	31.70
1,3-Butadiene-----	C_4H_6	0	12.16	12.20	14.59	16.97	19.18	21.19	23.01	24.66	26.16	27.54	28.80	29.96	31.03	32.02
1,2-Pentadiene-----	C_5H_8	0	16.2	16.3	19.3	22.3	25.0	27.6	29.9	32.0	34.0	35.8	37.4	39.0	40.4	41.7
<i>cis</i> -1,3-Pentadiene (<i>cis</i> -piperylene)-----	C_5H_8	0	14.5	14.6	17.5	20.5	23.4	26.0	28.5	30.7	32.7	34.6	36.3	37.9	39.4	40.7
<i>trans</i> -1,3-Pentadiene (<i>trans</i> -piperylene)-----	C_5H_8	0	15.3	15.4	18.6	21.7	24.5	27.1	29.5	31.7	33.7	35.5	37.2	38.7	40.1	41.4
1,4-Pentadiene-----	C_5H_8	0	16.5	16.6	19.6	22.4	25.2	27.7	29.9	32.0	34.0	35.8	37.4	39.0	40.4	41.7
2,3-Pentadiene-----	C_5H_8	0	15.7	15.8	18.6	21.4	24.0	26.5	28.8	31.0	33.0	34.8	36.5	38.1	39.5	40.9
3-Methyl-1,2-butadiene-----	C_5H_8	0	15.8	15.8	18.9	21.8	24.6	27.1	29.4	31.5	33.5	35.3	37.0	38.6	40.0	41.3
2-Methyl-1,3-butadiene (isoprene)-----	C_5H_8	0	15.0	15.1	18.4	21.7	24.6	27.3	29.7	31.9	33.8	35.7	37.4	38.9	40.3	41.6

TABLE 2. *Values of the free-energy function, for the ideal gaseous state, to 1,500° K, for the C₃ to C₅ diolefins*

Compound (gas)	For-mu-la	Temperature in ° K														
		0	298.16	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400	1,500
Free-energy function, (F° - H° ₀)/T, in cal/deg mole																
Propadiene (allene).....	C ₃ H ₄	0	-48.18	-48.24	-51.35	-54.08	-56.55	-58.85	-61.00	-63.02	-64.94	-66.76	-68.50	-70.16	-71.76	-73.29
1,2-Butadiene.....	C ₄ H ₆	0	-57.11	-57.19	-61.21	-64.79	-68.10	-71.19	-74.11	-76.88	-79.52	-82.04	-84.47	-86.80	-89.02	-91.18
1,3-Butadiene.....	C ₄ H ₆	0	-54.46	-54.54	-58.38	-61.89	-65.18	-68.29	-71.24	-74.05	-76.72	-79.28	-81.73	-84.09	-86.35	-88.52
1,2-Pentadiene.....	C ₅ H ₈	0	-63.5	-63.6	-68.7	-73.3	-77.6	-81.7	-85.5	-89.1	-92.6	-95.9	-99.1	-102.2	-105.1	-108.0
cis-1,3-Pentadiene (cis-piperylene).....	C ₅ H ₈	0	-62.9	-63.0	-67.6	-71.8	-75.8	-79.6	-83.3	-86.7	-90.1	-93.3	-96.4	-99.3	-102.2	-105.0
trans-1,3-Pentadiene (trans-piperylene).....	C ₅ H ₈	0	-61.1	-61.2	-66.1	-70.5	-74.7	-78.7	-82.5	-86.1	-89.5	-92.8	-96.0	-99.0	-101.9	-104.8
1,4-Pentadiene.....	C ₅ H ₈	0	-63.2	-63.3	-68.5	-73.1	-77.4	-81.5	-85.4	-89.0	-92.5	-95.8	-99.0	-102.0	-105.0	-107.8
2,3-Pentadiene.....	C ₅ H ₈	0	-61.9	-62.0	-66.9	-71.4	-75.5	-79.4	-83.1	-86.6	-90.0	-93.2	-96.3	-99.3	-102.2	-104.9
3-Methyl-1,2-butadiene.....	C ₅ H ₈	0	-60.6	-60.7	-65.7	-70.2	-74.5	-78.5	-82.2	-85.8	-89.2	-92.5	-95.7	-98.7	-101.6	-104.4
2-Methyl-1,3-butadiene (isoprene).....	C ₅ H ₈	0	-60.4	-60.5	-65.3	-69.8	-74.0	-78.0	-81.8	-85.4	-88.9	-92.2	-95.4	-98.4	-101.4	-104.2

TABLE 3. *Values of the entropy, for the ideal gaseous state, to 1,500° K, for the C₃ to C₅ diolefins*

Compound (gas)	For-mu-la	Temperature in ° K														
		0	298.16	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400	1,500
Entropy, S°, in cal/deg mole																
Propadiene (allene).....	C ₃ H ₄	0	58.30	58.39	62.89	67.02	70.83	74.36	77.65	80.73	83.61	86.33	88.90	91.33	93.64	95.83
1,2-Butadiene.....	C ₄ H ₆	0	70.03	70.15	76.28	81.95	87.25	92.20	96.85	101.22	105.34	109.22	112.91	116.42	119.72	122.88
1,3-Butadiene.....	C ₄ H ₆	0	66.62	66.74	72.97	78.86	84.36	89.48	94.25	98.71	102.88	106.82	110.53	114.05	117.38	120.54
1,2-Pentadiene.....	C ₅ H ₈	0	79.7	79.9	88.0	95.6	102.6	109.3	115.4	121.1	126.6	131.7	136.5	141.2	145.5	149.7
cis-1,3-Pentadiene (cis-piperylene).....	C ₅ H ₈	0	77.5	77.6	85.1	92.3	99.2	105.7	111.7	117.4	122.18	127.9	132.7	137.2	141.6	145.7
trans-1,3-Pentadiene (trans-piperylene).....	C ₅ H ₈	0	76.4	76.8	84.6	92.2	99.2	105.8	112.0	117.8	123.2	128.3	133.1	137.7	142.1	146.2
1,4-Pentadiene.....	C ₅ H ₈	0	79.7	79.9	88.1	95.5	102.6	109.2	115.3	121.0	126.5	131.6	136.4	141.0	145.3	149.5
2,3-Pentadiene.....	C ₅ H ₈	0	77.6	77.8	85.5	92.8	99.5	105.9	111.9	117.6	123.0	128.0	132.8	137.4	141.7	145.8
3-Methyl-1,2-butadiene.....	C ₅ H ₈	0	76.4	76.5	84.6	92.0	99.1	105.6	111.6	117.3	122.7	127.8	132.7	137.3	141.6	145.7
2-Methyl-1,3-butadiene (isoprene).....	C ₅ H ₈	0	75.4	75.6	83.7	91.4	98.6	105.3	111.5	117.3	122.7	127.9	132.7	137.3	141.7	145.8

TABLE 4. *Values of the heat content, for the ideal gaseous state, to 1,500° K, for the C₃ to C₅ diolefins*

Compound (gas)	For-mu-la	Temperature in ° K														
		0	298.16	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400	1,500
Heat content, (H° - H° ₀), in cal/mole																
Propadiene (allene).....	C ₃ H ₄	0	3017.4	3045.0	4616.0	6470.0	8568.0	10857.0	13328.0	15939.0	18680.0	21527.0	24480.0	27521.0	30632.0	33810.0
1,2-Butadiene.....	C ₄ H ₆	0	3852.2	3888.0	6028.0	8580.0	11490.0	14707.0	18192.0	21906.0	25820.0	29898.0	34128.0	38506.0	42980.0	47550.0
1,3-Butadiene.....	C ₄ H ₆	0	3625.6	3660.0	5836.0	8485.0	11508.0	14833.0	18408.0	22194.0	26160.0	30294.0	34560.0	38948.0	43442.0	48030.0
1,2-Pentadiene.....	C ₅ H ₈	0	4830	4890	7720	11150	15000	19320	23920	28800	34000	39380	44880	50700	56560	62550
cis-1,3-Pentadiene (cis-piperylene).....	C ₅ H ₈	0	4323	4380	7000	10250	14040	18200	22800	27630	32700	38060	43560	49270	55160	61050
trans-1,3-Pentadiene (trans-piperylene).....	C ₅ H ₈	0	4562	4620	7440	10850	14700	18970	23600	28530	33700	39050	44640	50310	56140	62100
1,4-Pentadiene.....	C ₅ H ₈	0	4920	4980	7840	11200	15120	19390	23920	28800	34000	39380	44880	50700	56560	62550
2,3-Pentadiene.....	C ₅ H ₈	0	4681	4740	7440	10700	14400	18550	23040	27900	33000	38280	43800	49530	55300	61350
3-Methyl-1,2-butadiene.....	C ₅ H ₈	0	4711	4740	7560	10900	14760	18970	23520	28350	33500	38830	44400	50180	56000	61950
2-Methyl-1,3-butadiene (isoprene).....	C ₅ H ₈	0	4472	4530	7360	10850	14760	19110	23760	28710	33800	39270	44880	50570	56420	62400

TABLE 5. *Values of the heat capacity, for the ideal gaseous state, to 1,500° K, for the C₃ to C₅ diolefins*

Compound (gas)	For-mu-la	Temperature in ° K														
		0	298.16	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400	1,500
Heat capacity, C _p ^o , cal/deg mole																
Propadiene (allene).....	C ₃ H ₄	0	14.10	14.16	17.21	19.82	22.00	23.84	25.42	26.80	28.00	29.04	29.96	30.75	31.45	32.06
1,2-Butadiene.....	C ₄ H ₆	0	19.15	19.23	23.54	27.39	30.72	33.54	36.01	38.16	40.02	41.62	43.02	44.23	45.29	46.20
1,3-Butadiene.....	C ₄ H ₆	0	19.01	19.11	24.29	28.52	31.84	34.55	36.84	38.81	40.52	42.02	43.32	44.47	45.47	46.34
1,2-Pentadiene.....	C ₅ H ₈	0	25.2	25.3	31.4	36.5	40.8	44.5	47.7	50.4	52.8	54.9	56.7	58.2	59.6	60.7
cis-1,3-Pentadiene (cis-piperylene).....	C ₅ H ₈	0	22.6	22.7	29.5	35.3	39.9	43.8	47.0	49.8	52.2	54.3	56.1	57.7	59.1	60.3
trans-1,3-Pentadiene (trans-piperylene).....	C ₅ H ₈	0	24.7	24.9	31.2	38.6	40.9	44.6	47.7	50.3	52.6	54.7	56.4	58.0	59.3	60.5
1,4-Pentadiene.....	C ₅ H ₈	0	25.1	25.2	31.3	36.5	40.8	44.4	47.6	50.3	52.7	54.7	56.5	58.1	59.4	60.6
2,3-Pentadiene.....	C ₅ H ₈	0	24.2	24.3	29.9	35.0	39.4	43.2	46.6	49.5	52.0	54.2	56.1	57.7	59.1	60.3
3-Methyl-1,2-butadiene.....	C ₅ H ₈	0	25.2	25.3	31.0	36.0	40.3	44.0	47.2	50.0	52.4	54.5	56.3	57.9	59.3	60.5
2-Methyl-1,3-butadiene (isoprene).....	C ₅ H ₈	0	25.0	25.2	31.8	37.1	41.4	45.0	48.0	50.6	52.9	54.9	56.6	58.2	59.5	60.6

2. Styrene and the Methylstyrenes

For styrene and the several methylstyrenes, the values of the heat-content function, free-energy function, and heat capacity were taken from reference [26]. As usual, the value of the entropy is given by the value of the heat-content function less the value of the free-energy function, and the

heat content is obtained by multiplying the value of the heat-content function by the temperature.

The resulting values of the thermodynamic functions for styrene and the methylstyrenes are given in tables 6 to 10, inclusive, which give values of the following properties, respectively, from 0° to 1,500° K: Heat-content function, free-energy function, entropy, heat content, and heat capacity.

TABLE 6. *Values of the heat-content function, for the ideal gaseous state, to 1,500° K, for styrene, C₈, and the methylstyrenes, C₉*

Compound (gas)	For-mu-la	Temperature in ° K														
		0	298.16	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400	1,500
Heat-content function, (H° - H ₀)/T, in cal/deg mole																
Ethenylbenzene (styrene; vinylbenzene; Phenylethylene).....	C ₈ H ₈	0	16.72	16.79	21.07	25.32	29.28	32.92	36.22	39.22	41.95	44.44	46.70	48.77	50.67	52.42
Isopropenylbenzene (α-methylstyrene; 2-phenyl-1-propene).....	C ₉ H ₁₀	0	20.3	20.3	25.2	30.0	34.6	38.8	42.6	46.1	49.3	52.2	54.9	57.3	59.6	61.6
cis-1-Propenylbenzene (cis-β-methylstyrene; cis-1-phenyl-1-propene).....	C ₉ H ₁₀	0	20.3	20.3	25.2	30.0	34.6	38.8	42.6	46.1	49.3	52.2	54.9	57.3	59.6	61.6
trans-1-Propenylbenzene (trans-β-methylstyrene; trans-1-phenyl-1-propene).....	C ₉ H ₁₀	0	19.9	20.0	25.1	30.0	34.6	38.9	42.7	46.2	49.5	52.4	55.1	57.5	59.8	61.8
1-Methyl-2-ethenylbenzene (o-methylstyrene).....	C ₉ H ₁₀	0	20.3	20.3	25.2	30.0	34.6	38.8	42.6	46.1	49.3	52.2	54.9	57.3	59.6	61.6
1-Methyl-3-ethenylbenzene (m-methylstyrene).....	C ₉ H ₁₀	0	20.3	20.3	25.2	30.0	34.6	38.8	42.6	46.1	49.3	52.2	54.9	57.3	59.6	61.6
1-Methyl-4-ethenylbenzene (p-methylstyrene).....	C ₉ H ₁₀	0	20.3	20.3	25.2	30.0	34.6	38.8	42.6	46.1	49.3	52.2	54.9	57.3	59.6	61.6

TABLE 7. *Values of the free-energy function, for the ideal gaseous state, to 1,500° K, for styrene, C₈, and the methylstyrenes, C₉*

Compound (gas)	For- mu- la	Temperature in ° K														
		0	298.16	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400	1,500
Free-energy function, (F° - H ₀ °)/T, in cal/deg mole																
Ethenylbenzene (styrene; vinylbenzene; phenylethylene)	C ₈ H ₈	0	-65.76	-65.86	-71.28	-76.44	-81.42	-86.21	-90.82	-95.26	-99.54	-103.66	-107.61	-111.44	-115.13	-118.68
Isopropenylbenzene (α-methylstyrene; 2-phenyl-1-propene)	C ₉ H ₁₀	0	-71.4	-71.5	-78.1	-84.2	-90.1	-95.8	-101.2	-106.4	-111.4	-116.3	-120.9	-125.4	-129.7	-133.9
cis-1-Propenylbenzene (cis-β-methylstyrene; cis-1-phenyl-1-propene)	C ₉ H ₁₀	0	-71.4	-71.5	-78.1	-84.2	-90.1	-95.8	-101.2	-106.4	-111.4	-116.3	-120.9	-125.4	-129.7	-133.9
trans-1-Propenylbenzene (trans-β-methylstyrene; trans-1-phenyl-1-propene)	C ₉ H ₁₀	0	-71.0	-71.1	-77.6	-83.7	-89.6	-95.3	-100.7	-105.9	-111.0	-115.8	-120.5	-125.0	-129.4	-133.5
1-Methyl-2-ethenylbenzene (o-methylstyrene)	C ₉ H ₁₀	0	-71.4	-71.5	-78.1	-84.2	-90.1	-95.8	-101.2	-106.4	-111.4	-116.3	-120.9	-125.4	-129.7	-133.9
1-Methyl-3-ethenylbenzene (m-methylstyrene)	C ₉ H ₁₀	0	-72.8	-72.9	-79.5	-85.6	-91.5	-97.2	-102.6	-107.8	-112.8	-117.7	-122.3	-126.8	-131.1	-135.3
1-Methyl-4-ethenylbenzene (p-methylstyrene)	C ₉ H ₁₀	0	-71.4	-71.5	-78.1	-84.2	-90.1	-95.8	-101.2	-106.4	-111.4	-116.3	-120.9	-125.4	-129.7	-133.9

TABLE 8. *Values of the entropy, for the ideal gaseous state, to 1,500° K, for styrene, C₈, and the methylstyrenes, C₉*

Compound (gas)	For- mu- la	Temperature in ° K														
		0	298.16	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400	1,500
Entropy, S°, in cal/deg mole																
Ethenylbenzene (styrene; vinylbenzene; phenylethylene)	C ₈ H ₈	0	82.48	82.65	92.35	101.76	110.70	119.13	127.04	134.48	141.49	148.10	154.31	160.21	165.80	171.10
Isopropenylbenzene (α-methylstyrene; 2-phenyl-1-propene)	C ₉ H ₁₀	0	91.7	91.8	103.3	114.2	124.7	134.6	143.8	152.5	160.7	168.5	175.8	182.7	189.3	195.5
cis-1-Propenylbenzene (cis-β-methylstyrene; cis-1-phenyl-1-propene)	C ₉ H ₁₀	0	91.7	91.8	103.3	114.2	124.7	134.6	143.8	152.5	160.7	167.5	175.8	182.7	189.3	195.5
trans-1-Propenylbenzene (trans-β-methylstyrene; trans-1-phenyl-1-propene)	C ₉ H ₁₀	0	90.9	91.1	102.7	113.7	124.2	134.2	143.4	152.1	160.5	168.2	175.6	182.5	189.2	195.3
1-Methyl-2-ethenylbenzene (o-methylstyrene)	C ₉ H ₁₀	0	91.7	91.8	103.3	114.2	124.7	134.6	143.8	152.5	160.7	168.5	175.8	182.7	189.3	195.5
1-Methyl-3-ethenylbenzene (m-methylstyrene)	C ₉ H ₁₀	0	93.1	93.2	104.7	115.6	126.1	136.0	145.2	153.9	162.1	169.9	177.2	184.1	190.7	196.7
1-Methyl-4-ethenylbenzene (p-methylstyrene)	C ₉ H ₁₀	0	91.7	91.8	103.3	114.2	124.7	134.6	143.8	152.5	160.7	168.5	175.8	182.7	189.3	195.5

TABLE 9. Values of the heat content, for the ideal gaseous state, to 1,500° K, for styrene, C₈, and the methylstyrenes, C₉

Compound (gas)	For- mula	Temperature in ° K														
		0	298.16	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400	1,500
Heat content ($H^\circ - H_0^\circ$), in cal/mole																
Ethenylbenzene (styrene; vinylbenzene; phenylethylene)-----	C ₈ H ₈	0	4,985	5,037	8,428	12,660	17,568	23,044	28,976	35,298	41,950	48,880	56,040	63,400	70,940	78,630
Isopropenylbenzene (α -methylstyrene; 2-phenyl-1-propene)-----	C ₉ H ₁₀	0	6,050	6,090	10,080	15,000	20,760	27,160	34,080	41,490	49,300	57,400	65,900	74,500	83,400	92,400
<i>cis</i> -1-Propenylbenzene (<i>cis</i> - β -methylstyrene; <i>cis</i> -1-phenyl-1-propene)-----	C ₉ H ₁₀	0	6,050	6,090	10,080	15,000	20,760	27,160	34,080	41,490	49,300	57,400	65,900	74,500	83,400	92,400
<i>trans</i> -1-Propenylbenzene (<i>trans</i> - β -methylstyrene; <i>trans</i> -1-phenyl-1-propene)-----	C ₉ H ₁₀	0	5,930	6,000	10,040	15,000	20,760	27,230	34,160	41,580	49,500	57,600	66,100	74,800	83,700	92,700
1-Methyl-2-ethenylbenzene (<i>o</i> -methylstyrene)-----	C ₉ H ₁₀	0	6,050	6,090	10,080	15,000	20,760	27,160	34,080	41,490	49,300	57,400	65,900	74,500	83,400	92,400
1-Methyl-3-ethenylbenzene (<i>m</i> -methylstyrene)-----	C ₉ H ₁₀	0	6,050	6,090	10,080	15,000	20,760	27,160	34,080	41,490	49,300	57,400	65,900	74,500	83,400	92,400
1-Methyl-4-ethenylbenzene (<i>p</i> -methylstyrene)-----	C ₉ H ₁₀	0	6,050	6,090	10,080	15,000	20,760	27,160	34,080	41,490	49,300	57,400	65,900	74,500	83,400	92,400

TABLE 10. Values of the heat capacity, for the ideal gaseous state, to 1,500° K, for styrene, C₈, and the methylstyrenes, C₉

Compound (gas)	Form- ula	Temperature in ° K														
		0	298.16	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400	1,500
Heat capacity, C_p° , in cal/deg mole																
Ethenylbenzene (styrene; vinylbenzene; phenylethylene)-----	C ₈ H ₈	0	29.18	29.35	38.32	45.94	52.14	57.21	61.40	64.93	67.92	70.48	72.66	74.54	76.16	77.57
Isopropenylbenzene (α -methylstyrene; 2-phenyl-1-propene)-----	C ₉ H ₁₀	0	34.7	34.9	44.8	53.5	60.7	66.8	71.8	76.1	79.8	82.9	85.6	87.9	89.9	91.6
<i>cis</i> -1-Propenylbenzene (<i>cis</i> - β -methylstyrene; <i>cis</i> -1-phenyl-1-propene)-----	C ₉ H ₁₀	0	34.7	34.9	44.8	53.5	60.7	66.8	71.8	76.1	79.8	82.9	85.6	87.9	89.9	91.6
<i>trans</i> -1-Propenylbenzene (<i>trans</i> - β -methylstyrene; <i>trans</i> -1-phenyl-1-propene)-----	C ₉ H ₁₀	0	34.9	35.1	45.2	54.0	61.2	67.2	72.2	76.4	80.0	83.1	85.8	88.1	90.0	91.7
1-Methyl-2-ethenylbenzene (<i>o</i> -methylstyrene)-----	C ₉ H ₁₀	0	34.7	34.9	44.8	53.5	60.7	66.8	71.8	76.1	79.8	82.9	85.6	87.9	89.9	91.6
1-Methyl-3-ethenylbenzene (<i>m</i> -methylstyrene)-----	C ₉ H ₁₀	0	34.7	34.9	44.8	53.5	60.7	66.8	71.8	76.1	79.8	82.9	85.6	87.9	89.9	91.6
1-Methyl-4-ethenylbenzene (<i>p</i> -methylstyrene)-----	C ₉ H ₁₀	0	34.7	34.9	44.8	53.5	60.7	66.8	71.8	76.1	79.8	82.9	85.6	87.9	89.9	91.6

IV. Heat of Formation, Free Energy of Formation, and Equilibrium Constant of Formation

For the standard heat of formation from the elements at 25° C, values for the diolefins, C₃ to C₅, were obtained as follows: 1,3-Butadiene, from reference [27]; 1,2-butadiene, from reference [28]; propadiene, *cis*- and *trans*-1,3-pentadiene, and 1,4-pentadiene, from combination of the data on heats of hydrogenation from references [36, 37] with the values for the heats of formation of the corresponding paraffin hydrocarbons from reference [29]; by calculation, using the relations between energy content and molecular structure given in references [29, 30, 31, 32, 33]. The values so calculated are believed to be uncertain by not more than about ±0.75 kcal/mole.

For the standard heat of formation from the elements at 25° C, values for styrene and the methylstyrenes were obtained as follows:

Ethenylbenzene (styrene, vinylbenzene, or phenylethylene), from reference [28]; isopropenylbenzene (α -methylstyrene or 2-phenyl-1-propene), from reference [34]; *cis*-1-propenylbenzene (*cis*- β -methylstyrene or *cis*-1-phenyl-1-propene), *trans*-1-propenylbenzene (*trans*- β -methylstyrene or *trans*-1-phenyl-1-propene), 1-methyl-2-ethenylbenzene (*o*-methylstyrene), 1-methyl-3-ethenylbenzene,

(*m*-methylstyrene), and 1-methyl-4-ethenylbenzene (*p*-methylstyrene) by calculation, using the relations between energy content and molecular structure given in references [29, 30, 31, 32, 33]. The values so calculated are believed to be uncertain by not more than about ±0.75 kcal/mole.

The method of calculating values of the standard heat of formation, the standard free energy of formation, and the logarithm of the equilibrium constant of formation for the different temperatures in the range 0° to 1,500° K, is the same as that described in section IV, 1, of reference [35].

The resulting values for the formation of the given hydrocarbon in the gaseous state, from the elements carbon (solid, graphite) and hydrogen (gaseous), each in its thermodynamic standard state, are presented in tables 11 to 16, inclusive, which give values of the following properties, for the C₃ to C₅ diolefins, styrene, and the methylstyrenes, to 1,500° K: Heat of formation, free energy of formation, and logarithm of the equilibrium constant of formation. It should be noted that the uncertainties in the values for the pentadienes and the methylstyrenes are such as to make the values of the logarithm (to the base 10) of the equilibrium constants of formation for these compounds uncertain by as much as 0.3 to 0.5, which is equivalent to a factor of 2 to 3 in the value of the equilibrium constant itself.

TABLE 11. *Values of the heat of formation, for the ideal gaseous state, to 1,500° K, for the C₃ to C₅ diolefins*

Compound (gas)	Formula	Temperature in ° K														
		0	298.16	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400	1,500
Heat of formation, ΔH_f° in kcal/mole																
Propadiene (allene)	C ₃ H ₄	47.70	45.92	45.91	45.35	44.85	44.42	44.03	43.71	43.44	43.23	43.06	42.94	42.84	42.75	42.68
1,2-Butadiene	C ₄ H ₆	42.78	39.55	39.53	38.56	37.78	37.09	36.50	36.03	35.66	35.40	35.21	35.10	35.04	35.00	34.99
1,3-Butadiene	C ₄ H ₆	30.20	26.75	25.83	25.80	25.12	24.53	24.05	23.67	23.37	23.17	23.04	22.96	22.91	22.89	22.89
1,2-Pentadiene	C ₅ H ₈	39.32	34.80	34.79	33.61	32.72	31.82	31.21	30.68	30.28	30.09	29.96	29.84	29.93	29.96	30.03
cis-1,3-Pentadiene (cis-piperylene)	C ₅ H ₈	23.73	18.70	18.69	17.29	16.16	15.27	14.49	13.97	13.52	13.19	13.04	12.93	12.91	12.97	12.93
trans-1,3-Pentadiene (trans-piperylene)	C ₅ H ₈	23.39	18.60	18.59	17.39	16.42	15.59	14.92	14.43	14.08	13.85	13.69	13.67	13.61	13.61	13.64
1,4-Pentadiene	C ₅ H ₈	29.63	25.20	25.19	24.04	23.01	22.25	21.59	21.00	20.59	20.40	20.27	20.15	20.24	20.27	20.34
2,3-Pentadiene	C ₅ H ₈	37.77	33.10	33.09	31.78	30.65	29.67	28.76	28.25	27.83	27.54	27.30	27.21	27.21	27.21	27.28
3-Methyl-1,2-butadiene	C ₅ H ₈	35.64	31.00	30.96	29.76	28.72	27.90	27.18	26.60	26.15	25.91	25.72	25.68	25.73	25.72	25.74
2-Methyl-1,2-butadiene (isoprene)	C ₅ H ₈	22.98	18.10	18.09	16.90	16.01	15.24	14.66	14.18	13.85	13.54	13.50	13.50	13.46	13.48	13.53

TABLE 12. *Values of the free energy of formation, for the ideal gaseous state, to 1,500° K, for the C₃ to C₅ diolefins*

Compound (gas)	Formula	Temperature in ° K														
		0	298.16	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400	1,500
Free energy of formation, ΔF_f° in kcal/mole																
Propadiene (allene)	C ₃ H ₄	47.70	48.37	48.38	49.29	50.33	51.48	52.68	53.93	55.23	56.50	57.86	59.25	60.62	61.98	63.35
1,2-Butadiene	C ₄ H ₆	42.78	48.21	48.26	51.32	54.60	58.03	61.57	65.18	68.85	72.55	76.26	80.01	83.75	87.50	91.25
1,3-Butadiene	C ₄ H ₆	30.20	36.43	36.49	39.88	43.47	47.20	51.02	54.90	58.82	62.78	66.74	70.72	74.70	78.67	82.66
1,2-Pentadiene	C ₅ H ₈	39.32	50.29	50.38	55.77	61.44	67.28	73.21	79.27	85.41	91.53	97.70	103.85	109.96	116.16	122.22
cis-1,3-Pentadiene (cis-piperylene)	C ₅ H ₈	23.73	34.88	34.97	40.61	46.60	52.77	59.09	65.44	71.98	78.44	84.97	91.50	98.14	104.77	111.13
trans-1,3-Pentadiene (trans-piperylene)	C ₅ H ₈	23.39	35.07	35.17	40.87	46.91	53.09	59.38	65.74	72.18	78.70	85.18	91.64	98.19	104.71	111.09
1,4-Pentadiene	C ₅ H ₈	29.63	40.69	40.78	46.16	51.85	57.71	63.66	69.66	75.81	81.94	88.12	94.28	100.53	106.61	112.83
2,3-Pentadiene	C ₅ H ₈	37.77	49.22	49.31	54.94	60.84	66.99	73.27	79.64	86.11	92.58	99.12	105.66	112.18	118.67	125.32
3-Methyl-1,2-butadiene	C ₅ H ₈	35.64	47.47	47.57	53.29	59.31	65.46	71.77	78.23	84.70	91.25	97.76	104.25	110.83	117.38	123.94
2-Methyl-1,2-butadiene (isoprene)	C ₅ H ₈	22.98	34.87	34.97	40.78	46.85	53.10	59.46	65.89	72.40	78.89	85.43	91.95	98.56	105.00	111.58

TABLE 13. *Values of the logarithm of the equilibrium constant of formation, for the ideal gaseous state, to 1,500° K, for the C₃ to C₅ diolefins*

Compound (gas)	Formula	Temperature in ° K														
		0	298.16	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400	1,500
Logarithm of equilibrium constant of formation, log ₁₀ K _f																
Propadiene (allene)-----	C ₃ H ₄	Infinite	-35.4519	-35.2462	-26.9316	-22.0008	-18.7503	-16.4479	-14.7338	-13.4123	-12.3488	-11.5024	-10.7904	-10.1907	-9.6747	-9.2306
1,2-Butadiene-----	C ₄ H ₆	do	-35.3377	-35.1597	-28.0379	-23.8644	-21.1356	-19.2218	-17.8050	-16.7181	-15.8564	-15.1512	-14.5710	-14.0790	-13.6600	-13.2943
1,3-Butadiene-----	C ₄ H ₆	do	-26.7004	-26.5796	-21.7868	-19.0023	-17.1941	-15.9302	-14.9974	-14.2834	-13.7205	-13.2602	-12.8799	-12.5573	-12.2809	-12.8070
1,2-Pentadiene-----	C ₅ H ₈	do	-36.861	-36.705	-30.469	-26.854	-24.507	-22.857	-21.655	-20.741	-20.004	-19.412	-18.913	-18.486	-18.134	-17.044
<i>cis</i> -1,3-Pentadiene (<i>cis</i> -piperylene)-----	C ₅ H ₈	do	-25.563	-25.477	-22.100	-20.367	-19.221	-18.448	-17.877	-17.479	-17.142	-16.882	-16.664	-16.499	-16.355	-16.191
<i>trans</i> -1,3-Pentadiene (<i>trans</i> -piperylene)-----	C ₅ H ₈	do	-25.707	-25.624	-22.332	-20.502	-19.337	-18.538	-17.959	-17.528	-17.199	-16.924	-16.689	-16.507	-16.346	-16.185
1,4-Pentadiene-----	C ₅ H ₈	do	-29.824	-29.712	-25.219	-22.663	-21.021	-19.875	-19.030	-18.410	-17.908	-17.508	-17.171	-16.901	-16.643	-16.439
2,3-Pentadiene-----	C ₅ H ₈	do	-36.074	-35.925	-30.017	-26.592	-24.401	-22.875	-21.756	-20.910	-20.233	-19.693	-19.243	-18.859	-18.526	-18.259
3-Methyl-1,2-butadiene-----	C ₅ H ₈	do	-34.797	-34.657	-29.114	-25.923	-23.843	-22.407	-21.371	-20.568	-19.942	-19.423	-18.986	-18.632	-18.324	-18.058
2-Methyl-1,3-butadiene(isoprene)-----	C ₅ H ₈	do	-25.560	-25.477	-22.284	-20.476	-19.341	-18.563	-18.000	-17.581	-17.241	-16.973	-16.746	-16.569	-16.392	-16.257

TABLE 14. *Values of the heat of formation, for the ideal gaseous state, to 1,500° K, for styrene, C₈, and the methylstyrenes, C₉*

Compound (gas)	Formula	Temperature in ° K														
		0	298.16	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400	1,500
Heat of formation, ΔH _f ° in kcal/mole																
Ethenylbenzene (styrene; vinylbenzene; phenylethylene)-----	C ₈ H ₈	40.34	35.22	35.19	33.83	32.72	31.81	31.08	30.51	30.09	29.83	29.69	29.63	29.61	29.63	29.68
Isopropenylbenzene (<i>α</i> -methylstyrene; 2-phenyl-1-propene)-----	C ₉ H ₁₀	33.33	27.00	26.94	25.23	23.80	22.66	21.73	20.99	20.45	20.13	19.93	19.90	19.83	19.95	19.93
<i>cis</i> -1-Propenylbenzene (<i>cis</i> - <i>β</i> -Methylstyrene; <i>cis</i> -1-phenyl-1-propene)-----	C ₉ H ₁₀	35.33	29.00	28.94	27.23	25.80	24.66	23.73	22.99	22.45	22.13	21.93	21.90	21.83	21.95	21.93
<i>trans</i> -1-Propenylbenzene (<i>trans</i> - <i>β</i> -methylstyrene; <i>trans</i> -1-phenyl-1-propene)-----	C ₉ H ₁₀	34.45	28.00	27.97	26.31	24.92	23.78	22.92	22.19	21.66	21.45	21.27	21.26	21.21	21.35	21.35
1-Methyl-2-ethenylbenzene (<i>o</i> -methylstyrene)-----	C ₉ H ₁₀	34.63	28.30	28.24	26.53	25.10	23.96	23.03	22.29	21.75	21.43	21.23	21.20	21.13	21.25	21.23
1-Methyl-3-ethenylbenzene (<i>m</i> -methylstyrene)-----	C ₉ H ₁₀	33.93	27.60	27.54	25.83	24.40	23.26	22.33	21.59	21.05	20.73	20.53	20.50	20.43	20.55	20.53
1-Methyl-4-ethenylbenzene (<i>p</i> -methylstyrene)-----	C ₉ H ₁₀	33.73	27.40	27.34	25.63	24.20	23.06	22.13	21.39	20.85	20.53	20.33	20.30	20.23	20.35	20.33

TABLE 15. *Values of the free energy of formation, for the ideal gaseous state, to 1,500° K, for styrene, C₈, and the methylstyrenes, C₉*

Compound (gas)	Formula	Temperature in ° K														
		0	298.16	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400	1,500
Free energy of formation, ΔF_f° in kcal/mole																
Ethenylbenzene (styrene; vinylbenzene; phenylethylene)	C ₈ H ₈	40.34	51.10	51.20	56.74	62.61	68.67	74.87	81.16	87.53	93.92	100.33	106.77	113.19	119.60	126.03
Isopropenylbenzene (α -methylstyrene; 2-phenyl-1-propene)	C ₉ H ₁₀	33.33	49.84	49.99	57.90	66.26	74.85	83.60	92.51	101.51	110.56	119.53	128.66	137.72	146.82	155.85
cis-1-Propenylbenzene (cis- β -methylstyrene; cis-1-phenyl-1-propene)	C ₉ H ₁₀	35.33	51.84	51.99	59.90	68.26	76.85	85.60	94.51	103.51	112.56	121.53	130.66	139.72	148.82	157.85
trans-1-Propenylbenzene (trans- β -methylstyrene; trans-1-phenyl-1-propene)	C ₉ H ₁₀	34.45	51.08	51.23	59.22	67.63	76.27	85.07	94.03	103.08	112.08	121.20	130.26	139.36	148.36	157.57
1-Methyl-2-ethenylbenzene (<i>o</i> -methylstyrene)	C ₉ H ₁₀	34.63	51.14	51.29	59.20	67.56	76.15	84.90	93.81	102.81	111.86	120.83	129.96	139.02	148.12	157.15
1-Methyl-3-ethenylbenzene (<i>m</i> -methylstyrene)	C ₉ H ₁₀	33.93	50.02	50.17	57.94	66.16	74.61	83.22	91.99	100.85	109.76	118.59	127.58	136.50	145.46	154.35
1-Methyl-4-ethenylbenzene (<i>p</i> -methylstyrene)	C ₉ H ₁₀	33.73	50.24	50.39	58.30	66.66	75.25	84.00	92.91	101.91	110.96	119.93	129.06	138.12	147.22	156.25

TABLE 16. *Values of the logarithm of the equilibrium constant of formation, for the ideal gaseous state, to 1,500° K, for styrene, C₈, and the methylstyrenes, C₉*

Compound (gas)	Formula	Temperature in ° K														
		0	298.16	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400	1,500
Logarithm of equilibrium constant of formation, $\log_{10} K_f$																
Ethenylbenzene (styrene; vinylbenzene; phenylethylene)	C ₈ H ₈	Infinite	-37.4532	-37.2963	-31.0030	-27.3649	-25.0117	-23.3762	-22.1729	-21.2543	-20.5264	-19.9330	-19.4456	-19.0295	-18.6705	-18.3630
Isopropenylbenzene (α -methylstyrene; 2-phenyl-1-propene)	C ₉ H ₁₀	do	-36.531	-36.416	-31.636	-28.963	-27.266	-26.101	-25.272	-24.649	-24.162	-23.749	-23.433	-23.153	-22.919	-22.707
cis-1-Propenylbenzene (cis- β -methylstyrene; cis-1-phenyl-1-propene)	C ₉ H ₁₀	do	-37.998	-37.874	-32.729	-29.837	-27.994	-26.726	-25.818	-25.134	-24.600	-24.146	-23.797	-23.490	-23.231	-22.998
trans-1-Propenylbenzene (trans- β -methylstyrene; trans-1-phenyl-1-propene)	C ₉ H ₁₀	do	-37.440	-37.320	-32.357	-29.562	-27.783	-26.560	-25.687	-25.030	-24.495	-24.081	-23.724	-23.429	-23.159	-22.958
1-Methyl-2-ethenylbenzene (<i>o</i> -methylstyrene)	C ₉ H ₁₀	do	-37.484	-37.384	-32.346	-29.531	-27.739	-26.560	-25.627	-24.965	-24.446	-24.007	-23.670	-23.352	-23.122	-22.896
1-Methyl-3-ethenylbenzene (<i>m</i> -methylstyrene)	C ₉ H ₁₀	do	-36.665	-36.548	-31.658	-28.919	-27.178	-25.982	-25.130	-24.488	-23.988	-23.562	-23.236	-22.948	-22.706	-22.488
1-Methyl-4-ethenylbenzene (<i>p</i> -methylstyrene)	C ₉ H ₁₀	do	-36.825	-36.708	-31.855	-29.138	-27.411	-26.226	-25.381	-24.746	-24.250	-23.828	-23.506	-23.220	-22.981	-22.765

V. Free Energies and Equilibria of Some Reactions of Isomerization and Dehydrogenation

In figure 1 are plotted, as a function of temperature, for the two butadienes, the amounts, in mole

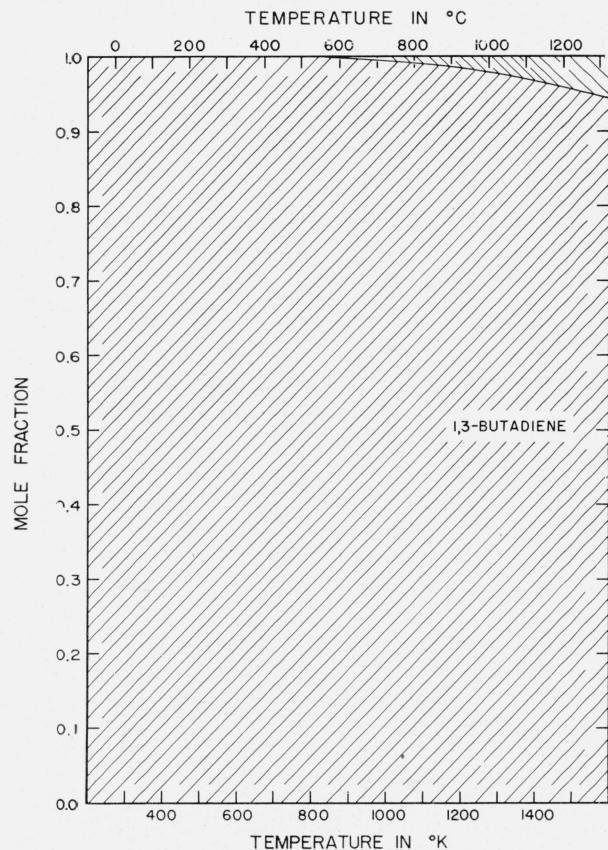


FIGURE 1. Equilibrium concentrations of the two butadienes.

The scale of ordinates measures the amount in mole fraction, and the scale of abscissas gives the temperature in degrees Kelvin and degrees Centigrade. The vertical width of a band at a given temperature measures the mole fraction of the given isomer present at equilibrium with all of its other isomers in the gaseous state.

fraction, of each of the isomers present at equilibrium with the other isomer in the gaseous state. The corresponding numerical values are given in table 17.

In figure 2 are plotted, as a function of temperature, for the seven pentadienes, the amounts, in mole fraction, of each of the isomers present at equilibrium with the other isomers in the gaseous state. The corresponding numerical values are given in table 18.

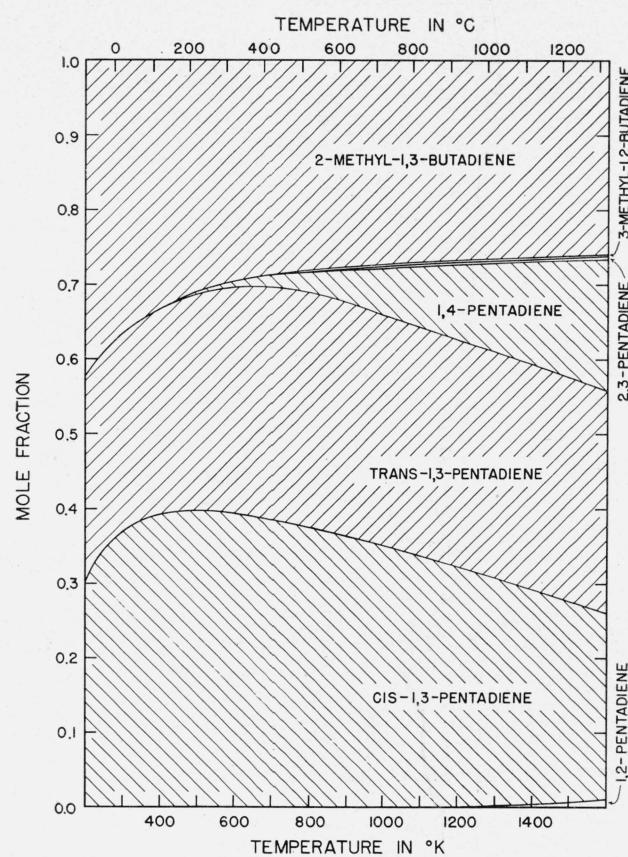


FIGURE 2. Equilibrium concentrations of the seven pentadienes.

The scale of ordinates measures the amount in mole fraction, and the scale of abscissas gives the temperature in degrees Kelvin and degrees Centigrade. The vertical width of a band at a given temperature measures the mole fraction of the given isomer present at equilibrium with all of its other isomers in the gaseous state.

TABLE 17. Equilibrium concentrations of the two butadienes in the ideal gaseous state to 1,500° K

Temperature °K	Composition, in mole fraction of the mixture of isomers at equilibrium	
	1,2-Butadiene	1,3-Butadiene
298.16	0.000	1.000
300	.000	1.000
400	.000	1.000
500	.000	1.000
600	.000	1.000
700	.001	.999
800	.002	.998
900	.004	.996
1,000	.007	.993
1,100	.013	.987
1,200	.020	.980
1,300	.029	.971
1,400	.040	.960
1,500	.053	.947

TABLE 18. Equilibrium concentrations of the seven pentadienes in the ideal gaseous state to 1,500° K

Temperature	Composition, in mole fraction, of the mixture of isomers at equilibrium						
	1,2-Pentadiene	cis-1,3-Pentadiene	trans-1,3-Pentadiene	1,4-Pentadiene	2,3-Pentadiene	3-Methyl-1,2-butadiene	2-Methyl-1,3-butadiene
° K							
298.16	0.000	0.367	0.263	0.000	0.000	0.000	0.370
300	.000	.369	.262	.000	.000	.000	.369
400	.000	.396	.285	.000	.000	.000	.319
500	.000	.398	.291	.002	.000	.000	.309
600	.000	.394	.301	.006	.000	.000	.299
700	.000	.382	.311	.014	.000	.000	.293
800	.000	.377	.312	.027	.000	.000	.284
900	.000	.357	.319	.042	.000	.000	.282
1000	.000	.351	.308	.060	.000	.001	.280
1100	.001	.338	.306	.080	.001	.001	.274
1200	.002	.323	.305	.100	.001	.002	.267
1300	.003	.308	.302	.122	.001	.002	.262
1400	.005	.286	.293	.148	.002	.003	.263
1500	.007	.287	.291	.162	.0035	.004	.246

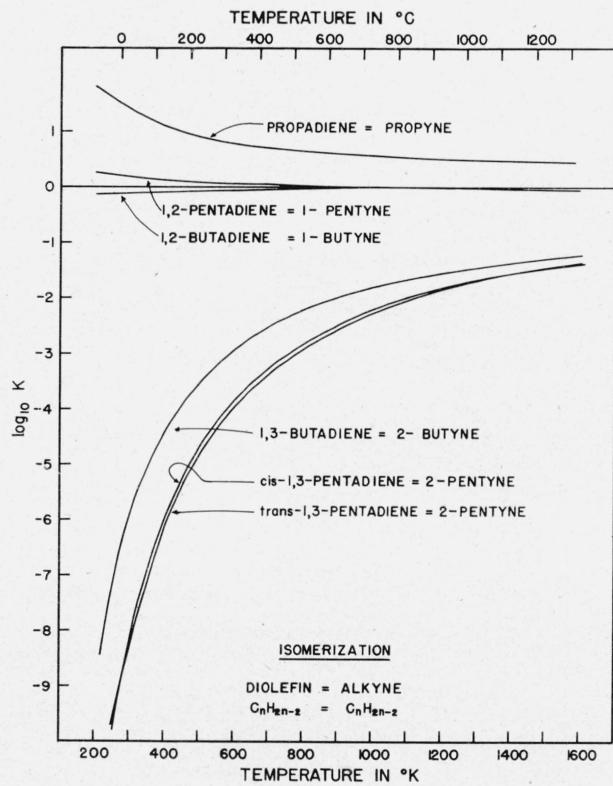


FIGURE 3. Dehydrogenation of monoolefins to diolefins.

The scale of ordinates gives the value of the logarithm (to the base 10) of the equilibrium constant for the reaction of dehydrogenating a given monoolefin to a given diolefin, in the gaseous state. The scale of abscissas gives the temperature in degrees Kelvin. The several curves refer to the following reactions in the gaseous state: A, Propylene=propadiene+hydrogen; B, 1-butene=1,3-butadiene+hydrogen; C, cis-2-butene=1,3-butadiene+hydrogen; D, trans-2-butene=1,3-butadiene+hydrogen; E, isobutene=1,3-butadiene+hydrogen.

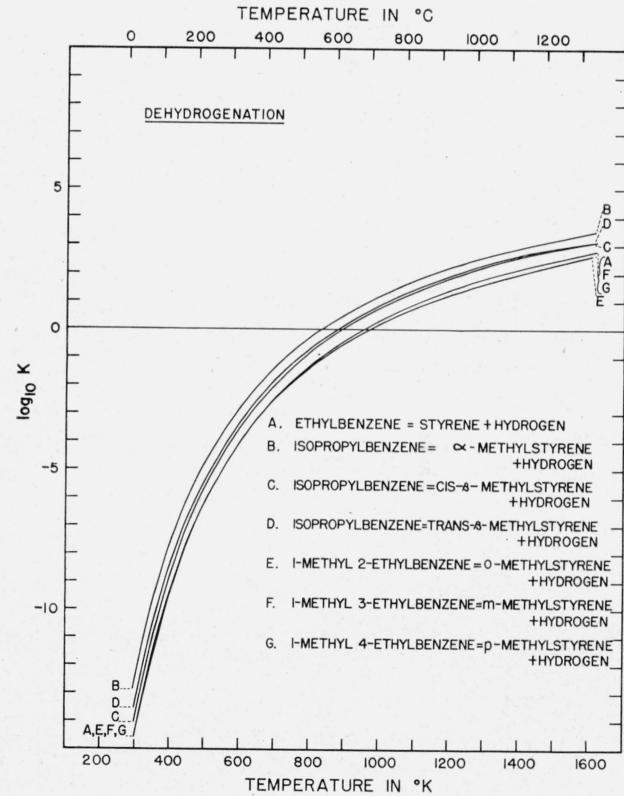


FIGURE 4. Isomerization of diolefins to acetylenes.

The scale of ordinates gives the value of the logarithm (to the base 10) of the equilibrium constant for the reaction of isomerization of a given diolefin to a given acetylene hydrocarbon, in the gaseous state. The scale of abscissas gives the temperature in degrees Kelvin. The several curves are for the following reactions in the gaseous state, as indicated: Propadiene=propyne; 1,2-butadiene=1-butyne; 1,2-pentadiene=1-pentyne; 1,3-butadiene=2-butyne; cis-1,3-pentadiene=2-pentyne; trans-1,3-pentadiene=2-pentyne.

TABLE 19. Equilibrium concentrations of the six methylstyrenes in the ideal gaseous state to 1,500° K

Temperature	Composition, in mole fraction, of the mixture of isomers, at equilibrium					
	α -Methylstyrene	<i>cis</i> - β -Methylstyrene	<i>trans</i> - β -Methylstyrene	<i>o</i> -Methylstyrene	<i>m</i> -Methylstyrene	<i>p</i> -Methylstyrene
$^{\circ}\text{K}$						
298.16	0.414	0.014	0.051	0.046	0.265	0.210
300	.396	.014	.049	.045	.293	.203
400	.329	.027	.062	.064	.319	.199
500	.292	.039	.073	.079	.322	.195
600	.265	.050	.081	.089	.325	.190
700	.247	.059	.086	.097	.325	.186
800	.234	.066	.090	.103	.325	.182
900	.224	.073	.093	.108	.323	.180
1,000	.215	.079	.096	.112	.322	.176
1,100	.208	.083	.100	.115	.320	.174
1,200	.202	.088	.103	.117	.319	.171
1,300	.198	.091	.105	.120	.318	.168
1,400	.192	.093	.110	.120	.319	.166
1,500	.191	.097	.107	.123	.315	.167

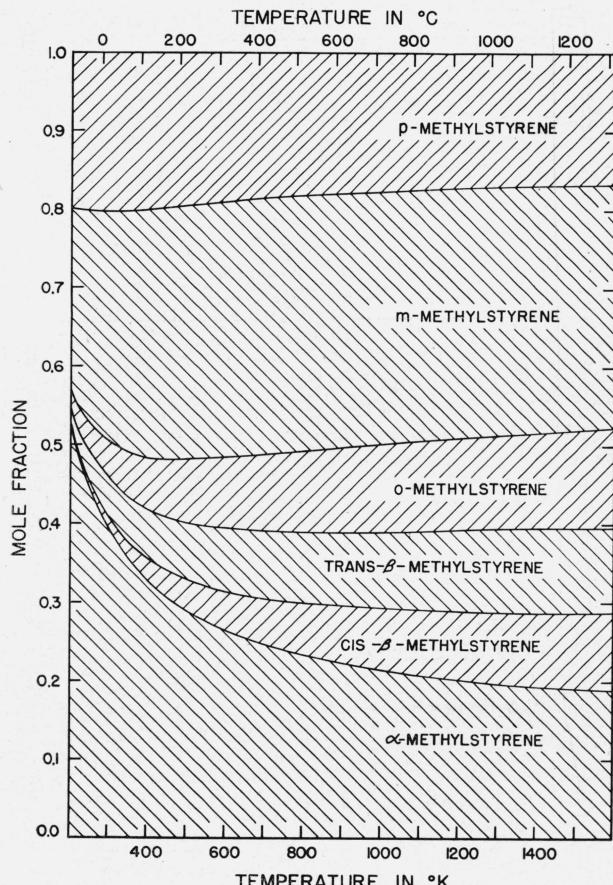


FIGURE 5.—Equilibrium concentrations of the six methylstyrenes.

The scale of ordinates measures the amount in mole fraction, and the scale of abscissas gives the temperature in degrees Kelvin and degrees Centigrade. The vertical width of a band at a given temperature measures the mole fraction of the given isomer present at equilibrium with all of its other isomers in the gaseous state.

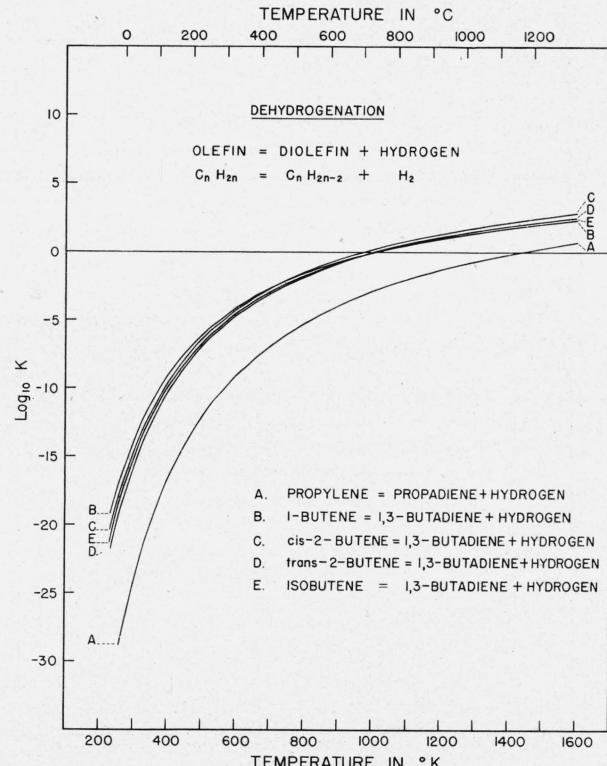


FIGURE 6. Dehydrogenation of alkylbenzenes to corresponding styrenes.

The scale of ordinates gives the value of the logarithm (to the base 10) of the equilibrium constant for the reaction of dehydrogenating a given alkylbenzene to a corresponding styrene, in the gaseous state. The scale of abscissas gives the temperature in degrees Kelvin. The several curves refer to the following reactions in the gaseous state: A, Ethylbenzene = styrene + hydrogen; B, isopropylbenzene = α -methylstyrene + hydrogen; C, isopropylbenzene = *cis*- β -methylstyrene + hydrogen; D, isopropylbenzene = *trans*- β -methylstyrene + hydrogen; E, 1-methyl-2-ethylbenzene = *o*-methylstyrene + hydrogen; F, 1-methyl-3-ethylbenzene = *m*-methylstyrene + hydrogen; G, 1-methyl-4-ethylbenzene = *p*-methylstyrene + hydrogen.

In figure 3 are plotted, as a function of temperature, values of the logarithm of the equilibrium constant for the reactions of dehydrogenation of propylene to propadiene and of each of the four butenes to 1,3-butadiene.

In figure 4 are plotted, as a function of temperature, values of the logarithm of the equilibrium constant for the reactions of isomerization of propadiene to propyne, 1,2-butadiene to 1-butyne, 1,2-pentadiene to 1-pentyne, 1,3-butadiene to 2-butyne, *cis*-1,3-pentadiene to 2-pentyne, and *trans*-1,3-pentadiene to 2-pentyne.

In figure 5 are plotted, as a function of temperature, for the six methylstyrenes, the amounts, in mole fraction, of each of the isomers present at equilibrium with the other isomers in the gaseous state. The corresponding numerical values are given in table 19.

In figure 6 are plotted, as a function of temperature, values of the logarithm of the equilibrium constant for the reactions of dehydrogenation of ethylbenzene to styrene, isopropylbenzene to α -methylstyrene, isopropylbenzene to *cis*- β -methylstyrene, isopropylbenzene to *trans*- β -methylstyrene, 1-methyl-2-ethylbenzene to *o*-methylstyrene, 1-methyl-3-ethylbenzene to *m*-methylstyrene, and 1-methyl-4-ethylbenzene to *p*-methylstyrene.

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